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On the structure near the short wavelength limit of the continuous X-ray spectrum

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With 6 figures in the text

ABSTRACT

Using a curved crystal spectrometer with good vacuum properties and cooled targets, the structure near the quantum limit of the continuous X-ray spectrum has been studied by the isochromat method. The isochromats of W, Ni, Cr (metals) and Cr_2O_3 (semiconductor) have been recorded at 5.4 kV. The W curve resolution has been improved and for Ni, Cr and Cr_2O_3 a foot structure near the limit observed. A shift of 1.5 V of the limit of Cr_2O_3 as compared to that of metallic Cr is reported. The fine structure and the shift support a certain interpretation of the structure, which is derived from consideration of the characteristic energy losses of the primary electrons and the density of states of the target material.

I. Introduction

An investigation has recently been carried out with the purpose of studying the spectral structure near the short wavelength limit of the continuous X-ray spectrum and, if possible, to make a redetermination of h/e. The investigation has been performed by Sandström and the result is now published [1]. A high X-ray intensity of the isochromats is the principal requirement for an accurate determination of this kind. In comparison with earlier work, Sandström got a surprisingly high intensity, which made rapid recording possible and revealed a fine structure with good reproducibility. However, all the isochromats had been measured with the use of a hot target. Since a comparison with measurements using a cold target is of interest, such an experiment was recently started. It was performed with an efficiently cooled tungsten target. The result agreed with that of Sandström. Even the initial curves were characterized by high intensity and good resolution. This encouraged further examination of the limit structure. The present paper gives the first results from the investigation.

II. Experimental conditions

The curved crystal spectrometer has been described in a recent paper [2]. The same topaz crystal and Geiger–Müller tube was suitable for use in the present experiment. To reduce the background the counter was surrounded by lead shielding. The manually operated scaler was replaced by an automatic one (EKCO Type N530F).

The resolving power of the spectrometer could be estimated from the width of the reference line Cr $K\alpha_1$. The full width at half maximum intensity of this line was 2.6 V. Its natural width is determined to 1.9 V [3]. Hence, according to "the square relation", the spectral band entering the counter had a breadth of 1.8 V.

All the recordings have been made at the same voltage, about 5400 V. The well smoothed and stabilized high voltage was delivered by circuits earlier described [4]. The ripples were continuously studied in an oscilloscope, the peak-to-peak voltage being less than 0.07 V. No absolute measuring of the voltage has been performed.

A tungsten filament was employed as cathode. It is more durable than an oxide cathode and gives a higher and more stable emission current, 20 mA in our case. The drawback of a directly heated cathode is the potential drop across the wire, causing a "smoothing out" of the structure to be studied [5]. In our apparatus this effect has been reduced to a minimum. The voltage drop across the actual emitting part of the wire was only about 0.3 V [4]. The sharpness of the cut off in the isochromats (see e.g. Fig. 1) confirms the unipotential character of the cathode.

The most essential problem in structure analysis of the present kind is contamination of the target. Recordings with a cold target require extremely high purity conditions in the X-ray tube. The spectrometer has gradually been rebuilt in order to meet these demands. Its acquired good properties in this respect are due to: (1) a large distance between cathode and target (25 cm); a magnetic lens had to be inserted for focusing and proper deflection of the electron beam; (2) a small X-ray tube volume to evacuate; and, (3) an effective pumping system. The resulting purity (vacuum $\leqslant 10^{-6}$ mm Hg) was best demonstrated by the reproducibility of the fine structure in the curves.

III. The isochromat curves

All the isochromats have been recorded at the wavelength of Cr $K\alpha_1$ 2285 XU, corresponding to a threshold voltage of about 5420 V.

The voltage has been varied in intervals of $\frac{1}{2}$, 1 or 2 V according to circumstances. As is stressed below the half-volt steps are of importance when a fine structure exists. The high intensity made possible rapid recording (2–3 hours) and sufficiently good statistics. The counting time per point was 200 or 300 sec. The standard deviation is indicated in the figures.

Prerequisite to the following considerations we need a reference point for voltage indications. As seen from the figures we have chosen a value, called "cut-off" voltage, the extrapolated point of intersection initial slope with the background, as indicated in the figures.

A. *Tungsten*

The target consisted of an analytically pure tungsten plate, 1 mm thick, which was tightly fastened to the watercooled copper holder.

The tungsten isochromat is now a standard curve. Its general appearance is well determined from the latest works [5, 6, 7]. The structural details, however, differ from author to author. One of our recordings is shown in Fig. 1 and it is in good agreement with the fine structure as reported by Sandström [1] using an oxide cathode and a hot target. It appears that the present curve is somewhat better resolved. The nearly symmetric main peak, recorded in $\frac{1}{2}$-volt steps, has its maximum

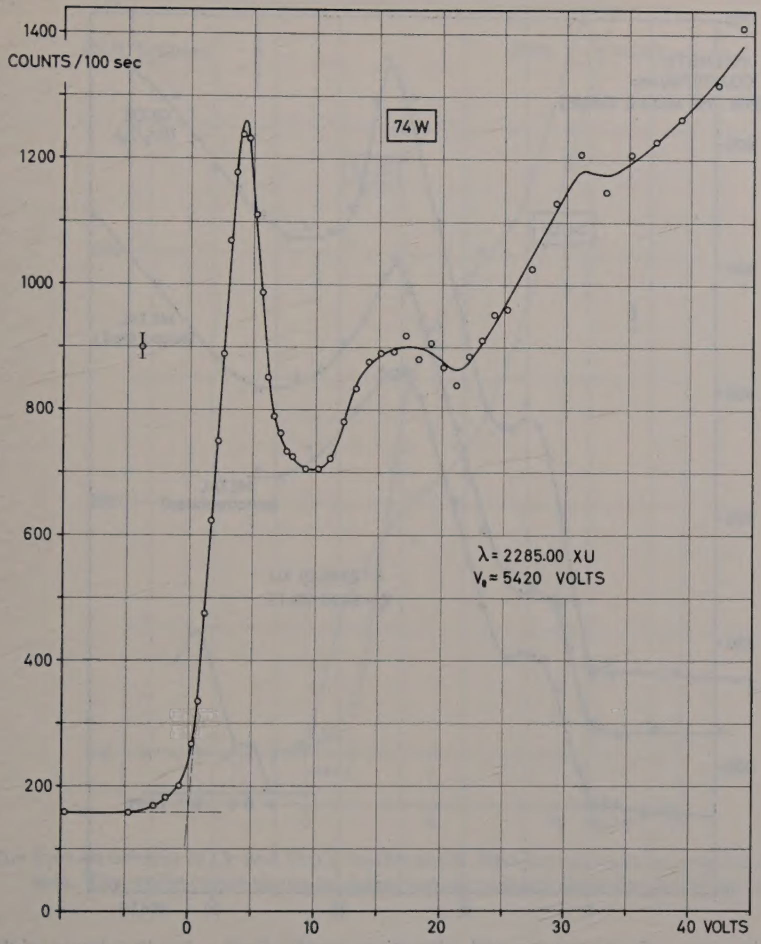

Fig. 1. Isochromat of tungsten.

intensity 4.3 V from the cut-off point. After the first peak the structure is characterized by two maxima, the positions of which can be determined to within one volt, to be 17 and 31 V above the cut-off voltage.

B. *Chromium*

The metallic chromium targets were of two types: (1) chromium electroplated and (2) chromium films evaporated onto a copper target. The evaporation was performed in the X-ray tube.

In the chromium isochromats a fine structure not observed before has been revealed. As is shown from Fig. 2, it appears near the break of the curves. This foot structure was reproducible with both types of targets and has been examined in detail. The result is given in Table 1, where the voltage differences between the cut-

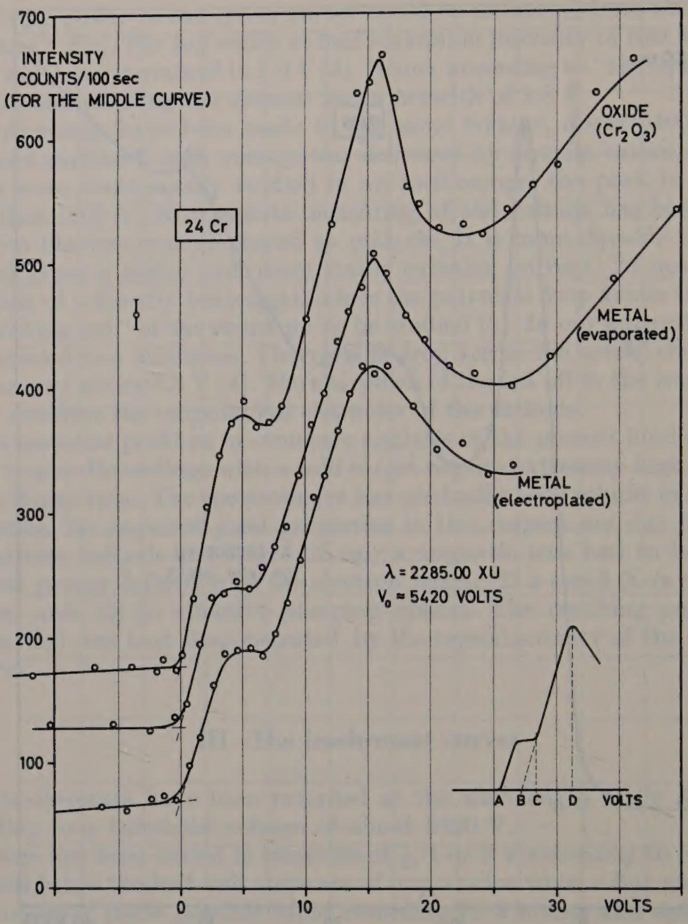

Fig. 2. Isochromats of chromium and chromium oxide Cr_2O_3. In the lower right hand corner is shown a schematic figure of the isochromats and the notation used.

Table 1. Voltage differences in the structure of the Cr isochromats.

For notation, see Fig. 2.

No.	Type of target	AB	AC volts	AD
1	Electroplated	3.6	7.0	15.6
2	Electroplated	4.0	6.9	15.6
3	Evaporated	3.5	6.6	15.6
4	Evaporated	3.5	6.7	15.8
5	Evaporated	3.7	6.8	15.0
	Mean	3.7	6.8	15.5

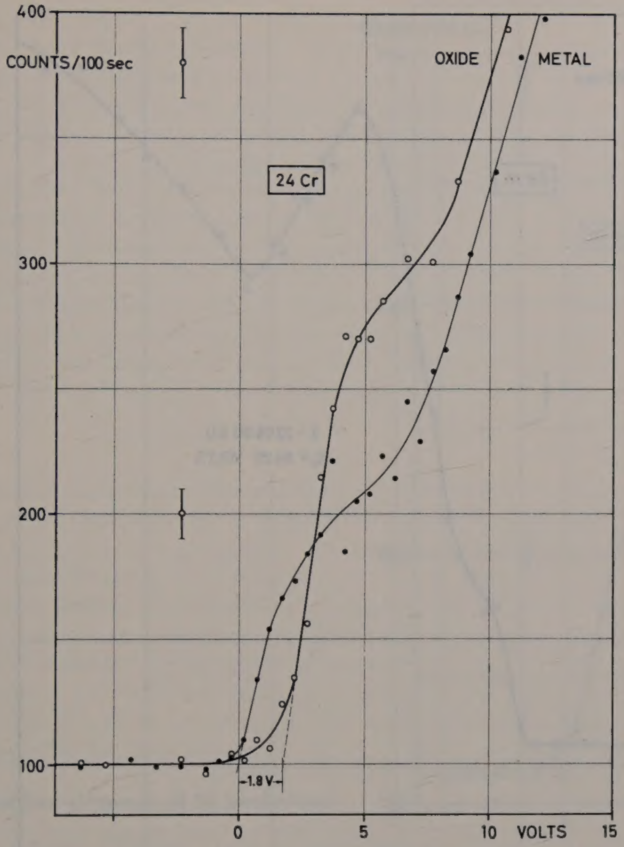

Fig. 3. The foot structures of Cr and Cr_2O_3 isochromats. The curves were recorded in rapid sucession. The oxide curve shows a higher cut-off voltage than the metal curve.

off point *A* and the characteristic points in the structure are inserted. The notation refers to the schematic figure in the lower right hand corner of Fig. 2. That the relatively pronounced structure, about 4 V wide, has escaped earlier detection must be due to contamination effects and too large voltage intervals between the measuring points. Disregarding the foot structure, the curves are of known shape with a maximum at 15.5 V (see Table 1) and a minimum at about 25 V above the limit.

C. *Chromium oxide*, Cr_2O_3

In an earlier paper [2], the author reported a series of measurements on chromium oxide. The studied *K* excitation curves of the oxide, which also are isochromats, differed essentially from those of the metal and also a chemical shift of the *K* excitation potential was found. A similar investigation at the short wavelength limit has been performed by the author and is here presented. The result is interesting. The shape of the oxide isochromats here agrees closely with that of the metal (Fig. 2). The resemblance was so complete that the surface layer was suspected to be metallic.

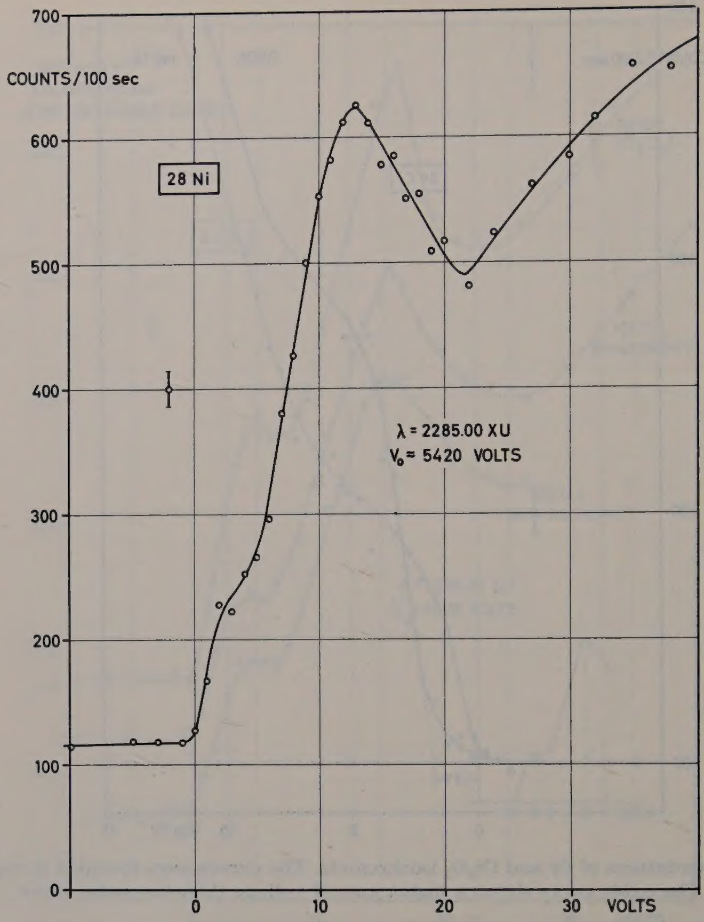

Fig. 4. Isochromat of nickel.

However, the results were confirmed by recordings of isochromats both at the high frequency limit and at the excitation threshold with the same target.

As seen from Fig. 2, the oxide gave a higher intensity than the metal. The curves in the figure are displaced vertically—in reality they have the same background—and horizontally to a common zero point to show the agreement in shape. In fact, a shift has been observed in the position of the isochromats. The cut-off voltage of the oxide is higher than that of the metal. Fig. 3 shows one of these shift determinations. The curves were recorded in rapid succession, first the oxide and then the metal evaporated from the furnace in the X-ray tube. The oxide layers were prepared as in reference [2] and were about 1000 Å thick. The size of the shift amounts to 1.5 V. As this value is an average of only three values (1.1, 1.7 and 1.8 V) it is only approximate.

An interesting observation can be made from the Cr-metal curve in Fig. 3. By choosing every four points we get a 2-volt interval curve, the usual type in earlier work. In the most unfavourable cases the cut-off point of the "new" curves shifts

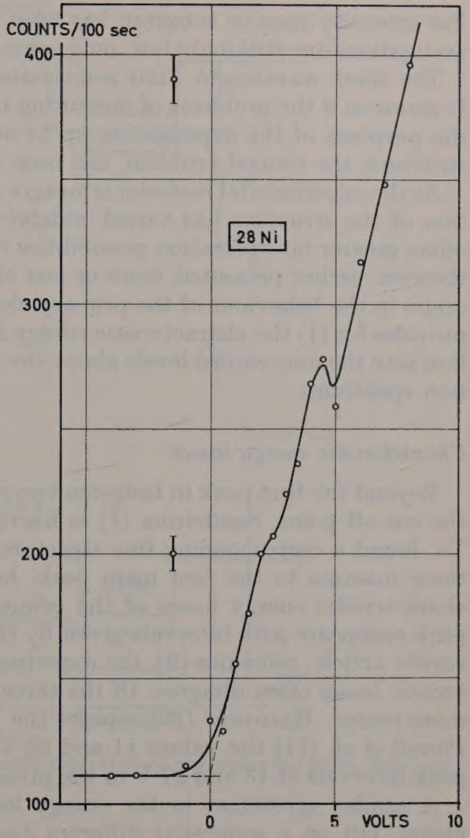

Fig. 5. The foot structure of Ni isochromat.

between $\frac{1}{2}$ and 1 V towards lower voltage and an appreciable contribution to the well-known "discrepancy" in the h/e determinations from the limit can be expected. This stresses the importance of varying the voltage in small steps.

D. *Nickel*

The first preliminary results for nickel may also be presented. As target an electrolytical deposit of nickel was employed. As is seen in Fig. 4, the isochromats of nickel show a structure similar to that of chromium. Bearden and Schwarz [5] have presented a nickel curve recorded at 9860 V which is in good agreement with ours. In comparison with chromium the foot structure, recorded in detail in Fig. 5, has a smaller extent ($AB \approx 2$ V and $AC \approx 5$ V). Also the main maximum and minimum have shifted slightly to lower voltages by the amounts of 13 V and 22 V respectively. It may be observed that, with identical recording conditions, the intensity of the main peaks of chromium and nickel is only half as large as that of tungsten.

IV. Interpretations of the isochromats

The structure near the quantum limit was first observed by Ohlin in 1942 [8]. Since then the main features of the structure for a few elements have been explored.

For intensity reasons tungsten has been the most popular target. However, the investigations are strikingly few, only some five, and no systematic study exists.

The short wavelength limit is intimately connected to a method of evaluating h/e. It seems as if the problems of measuring this constant with precision have dominated the purposes of the experiments up to now, while the question of the origin of the structure, the central problem, has been neglected.

As the experimental material is meagre and the resolution often bad, the interpretation of the structure has varied widely. The good resolution of the present curves offers greater interpretation possibilities than before. Our results give support to two theories, earlier presented more or less clearly. The isochromats seem to have their origin in the behaviour of the primary electrons in the target material. The structure provides for (1) the characteristic energy losses of these electrons, and (2) their transition into the unoccupied levels above the Fermi level (compare a usual X-ray absorption spectrum).

Characteristic energy losses

Beyond the first peak in tungsten two maxima were observed at 17 and 31 V above the cut-off point. Sandström [1] in his recordings of the isochromats of W, Mo and Ta, found a corresponding fine structure. By measuring the voltage intervals from these maxima to the first main peak, he could identify these differences with the characteristic energy losses of the primary electrons in the actual target; thus the peak reappears with intervals given by the losses. However, as can be seen from the review article, reference [9], the experimental results in the consideration of characteristic losses often disagree. Of the three determinations made for tungsten, two are more recent. Harrower [10] reports the first loss values to be 15 and 27 V, while Powell *et al.* [11] the values 11 and 25 V. These figures may be compared with the peak intervals of 13 and 27 V in the present work (Fig. 1).

A similar agreement in the energy loss values was observed for chromium and nickel, but on a somewhat different basis. The general shape and position of the main peak for these metals differ essentially from those of tungsten. According to reference [9] the first retardation maximum, agreeing in different investigations, appears after 22–26 V for Cr and 22–23 V for Ni. The corresponding region of the isochromats, about 40 V above the break, has not been explored. However, as pointed out by Albert [6], the intensity minima must also refer to the energy losses as they represent the reappearance of the very limit. Consequently, we may expect the first minima of the two metals at distances, given by the figures above as measured from the cut-off points. The observed values 25 V for Cr and 22 V for Ni confirm this hypothesis.

The density of states

By the very assumption of the characteristic losses, the energy distribution of the electron beam is supposed to be monochromatic in a voltage region determined by the first energy loss. Now we shall further assume that the final states of the primary electrons are the unoccupied levels above the Fermi level. Then the density of states of the target material is given by the isochromat structure below the first minimum, where overlapping sets in.

The selection rules governing the transitions of the electrons into the conduction band must be of special importance for the interpretation of the structure. No such

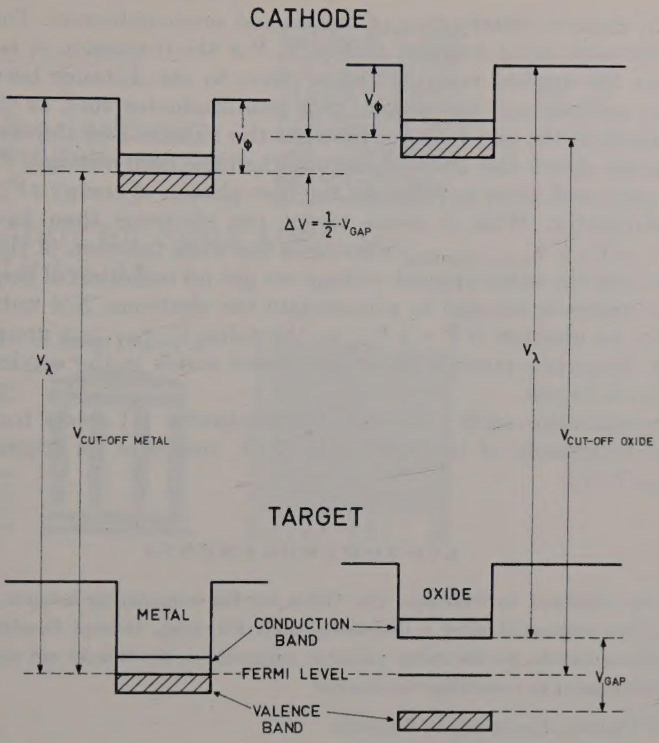

Fig. 6. Schematic level diagram illustrating the interpretation of the observed shift. See text.

selection rules are known and the experimental data up to now is too limited to allow any conclusions. For the present we confine ourselves to some remarks of the present results.

It is interesting to note that the revealed foot structure in Cr is somewhat larger than that of Ni and, according to Bearden and Schwarz [5], disappears in Cu. These facts suggest its arising from the empty $3d$ band. The dominating peak in W has earlier been identified by Ulmer and Vernickel [7] with the pronounced maximum near the edge in L_{II} and L_{III} absorption spectra of the element [12]. The peak has been ascribed to the unfilled $5d$ band.

For chromium and its oxide, Cr_2O_3, the isochromats may be compared with the corresponding K-excitation curves in reference [2]. In the latter type of absorption curves the density of states has p-character. Now the diversity in shape is most apparent. The characteristic minimum of the oxide and the definite intensity increase beyond the plateau in the metal have no correspondence in the present oxide and metal curves. On the contrary, the latter two are quite similar in shape (Fig. 2). Compare in this respect the resemblance between the $L_{II,III}$ absorption curves of metallic W with those of the oxide WO_3 [12].

Chromium oxide was found to require a higher cut-off voltage than the metal (Fig. 3). This result gives a strong support to the assumption that the isochromats indicate the density of states near the Fermi level. The shift is expected from the difference in electron distribution of metals and semiconductors. This is understood from the schematic level diagram in Fig. 6. For the discussion it is essential to remember that the applied voltage always refers to the distance between the Fermi levels in the cathode and the target. In a semiconductor such as Cr_2O_3, the Fermi level is situated in the gap halfway between the valence and the conduction bands.

The diagram shows the level situation when the limit voltage, $V_{\text{cut-off}}$ is reached in the two cases and when in principle the first photon of energy eV_λ is registered by the monochromator. With a metal target the electrons then have a maximum potential $V_\lambda = V_\phi + V_{\text{cut-off (metal)}}$, where ϕ is the work function of the cathode. With oxide target and the same applied voltage we get no radiation of requisite energy as there are no states in the gap to accomodate the electrons. Not until the voltage is increased by an amount $\Delta V = \frac{1}{2} V_{\text{gap}}$ to the value $V_{\text{cut-off (oxide)}}$ are photons of sufficiently high frequency received from the lowest states in the conduction band and the radiation is begun.

The "contamination shift" reported by Sandström [1] seems to be of the same nature. The magnitude of the shift, 4 to 5 eV, indicates its origin from a carbon layer ($V_{\text{gap}} \approx 7$ eV).

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